

SUPPORTING INFORMATION FOR:

# Decoupling H<sub>2</sub>(g) and O<sub>2</sub>(g) Production in Water Splitting by a Solar-Driven

## V<sup>3+/2+</sup>(aq,H<sub>2</sub>SO<sub>4</sub>)|KOH(aq) Cell

*Alec Ho<sup>1</sup>, Xinghao Zhou<sup>2</sup>, Lihao Han<sup>1</sup>, Ian Sullivan<sup>1</sup>, Christoph Karp<sup>1</sup>, Nathan S.*

*Lewis<sup>1, 3, 4\*</sup>, Chengxiang Xiang<sup>1\*</sup>*

<sup>1</sup> Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA

<sup>2</sup> Division of Engineering and Applied Science, Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, CA 91125, USA

<sup>3</sup> Beckman Institute Molecular Materials Research Center, California Institute of Technology, Pasadena, CA 91125, USA

<sup>4</sup> Kavli Nanoscience Institute, California Institute of Technology, Pasadena, CA 91125, USA

\*To whom correspondence should be addressed: [nslewis@caltech.edu](mailto:nslewis@caltech.edu), [cxx@caltech.edu](mailto:cxx@caltech.edu)

## Experimental Procedures

### Materials

All chemical reagents were used without further purification. The anolyte was prepared with 2.5 M KOH(aq) ( $\geq 85\%$ , Macron). For the catholyte, a solution of 0.36 M  $V^{4+}$  was prepared from  $VOSO_4 \cdot xH_2O$  (97%,  $x=3.41$ , Sigma-Aldrich) in 2.0 M  $H_2SO_4$ (aq) by diluting ultrapure, concentrated sulfuric acid  $H_2SO_4$  (93-98%, J.T. Baker) in ultrapure water (18.2 M $\Omega$  cm resistivity). 0.36 M  $V_2(SO_4)_3$  in 2.0 M  $H_2SO_4$ (aq) was obtained by reducing  $V^{4+}$  to  $V^{2+}$ , followed by oxidizing  $V^{2+}$  to  $V^{3+}$  by bubbling with oxygen ( $O_2$ , Air Liquide) for  $< 30$  min. The cathodic solution was deoxygenated in the cathodic half-cell for at least 10 min with in-house nitrogen ( $N_2$ ) before the charging process.  $Mo_2C$  (99.5%, Strem) catalyst powder was used for  $H_2(g)$  production from  $V^{2+}$  in  $H_2SO_4$ .

### Redox Cell

The electrochemical cell consisted of two 3-necked glass half cells, an O-ring, a gasket, and a bipolar membrane with a geometric area of 6.0 cm<sup>2</sup> (fumasep FBM, FuMA-Tech GmbH). The electrode in the cathodic half-cell was a carbon fiber cloth with a geometric area of 6.0 cm<sup>2</sup> (FuelCellsEtc), and the electrode in the anodic half-cell was a Ni mesh with a geometric area of 6.0 cm<sup>2</sup> (Sigma Aldrich).

### Electrochemical charging experiments

During charging and discharging,  $H_2(g)$  production was measured with a differential pressure manometer (HD755, Extech). EC-lab was used to measure the charge of the cell.

Beginning with solutions of 50.0 mL 0.36 M  $V_2(SO_4)_3$ , 2.0 M  $H_2SO_4(aq)$  ( $pH = -0.16$ ), varying degrees of charge were passed to obtain solutions of various ratios of  $V^{2+}/V^{3+}$  in  $H_2SO_4(aq)$ . 6.0 mL of the partially charged solution was added to a flask and then purged with  $N_2(g)$ . The flask was sealed to a compartment that contained 0.50 g  $Mo_2C$  powder, with the compartment also connected to a differential pressure manometer. To proceed with the measurement, the catalyst powder was mixed with the partially charged solution and the suspension was stirred at 400 rpm. While the stirring of the catholyte influenced the initial hydrogen release rate, the overall hydrogen collected after 5 min was independent of the rate of stirring. The manometer measured the amount of  $H_2(g)$  produced over time, recording data every 1 s.

### **Bipolar membrane measurements**

The current density vs. voltage behavior of the bipolar membrane was measured with a four-point measurement configuration.<sup>1</sup> Various current densities were applied to the cell using two Pt mesh electrodes, one as the cathode and one as the anode, and two Ag/AgCl reference electrodes were used to measure the potential near the membrane.

### **Ion crossover measurements**

The concentrations of  $V^{3+/2+}$  in the anolyte before and after a continuous operation of 10 mA  $cm^{-2}$  for 24 hours were determined using inductively coupled plasma mass spectroscopy (Agilent 8800 ICP-MS Triple Quad), and the concentrations of  $K^+$  in the catholyte and  $SO_4^{2-}$  in the anolyte were determined using ion chromatography (IC, Dionex ICS-2000 Ion Chromatography System). Table S2 lists the concentration of  $V^{3+/2+}$  with

known concentrations (1, 10, 50, 100, 500  $\mu\text{M}$ ) as well as the measured concentration in the anolyte samples. The five measured concentrations were very close to the known values, confirming the accuracy of the measurement for the vanadium concentration in the anolyte samples before and after operating for 24 hours.

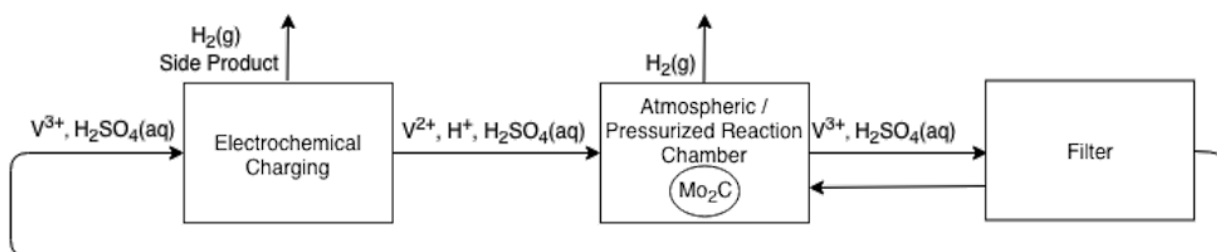
### **Outdoor charging experiments**

The vanadium redox cell was placed in series with a 16% efficient polycrystalline photovoltaic module (Sundance Solar) affixed to a dual-axis smart solar tracker (Fuel Cell Store). The illumination intensity was measured with a photodiode (Thorlabs). Fresh catholyte was charged over the course of a day to 85-86% charge capacity, and all 50 mL of the charged solution was combined with  $\text{Mo}_2\text{C}$  to generate  $\text{H}_2(\text{g})$ . The discharged solution was passed through a 0.45  $\mu\text{m}$  syringe filter (PALL) followed by a 0.2  $\mu\text{m}$  syringe filter (PALL) and reused in the system.

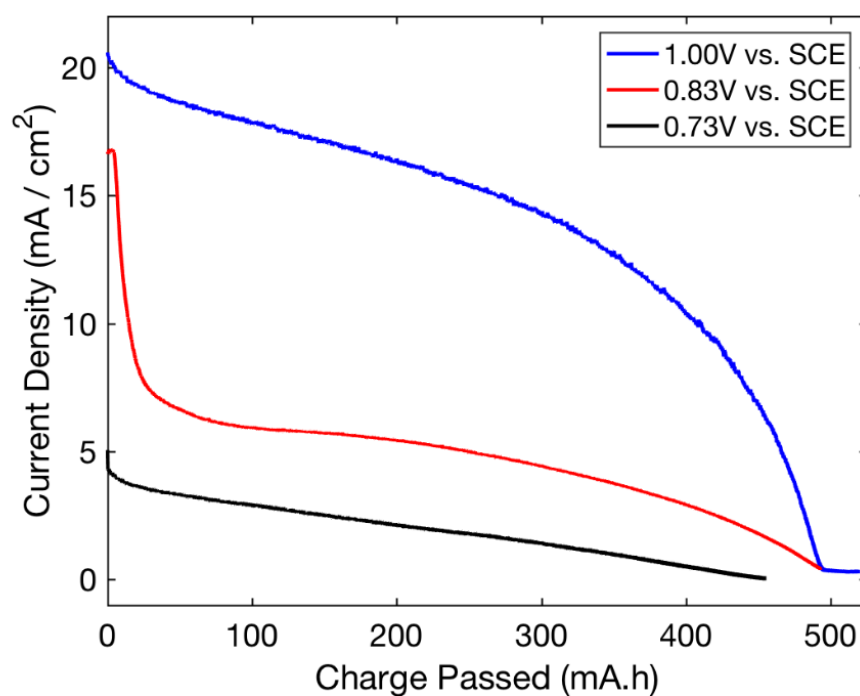
### **Pressurization experiments**

In the pressurization experiment apparatus, a stainless-steel tube was used as the reaction vessel. A plastic tube closed off at one end contained  $\text{Mo}_2\text{C}$  catalyst and another portion of the system had 25.0 mL of catholyte solution. The chamber was connected to the rest of the apparatus, and the whole apparatus was filled with hydrogen gas to various pressures (1 atm, 10 atm and 100 atm). After pressurization, the hydrogen tank was detached, the valve to the pressure gauge was temporarily closed, and the apparatus was rotated upside down to allow the catholyte to mix with the catalyst. This rotation, along with some shaking of the apparatus, was repeated several times to ensure sufficient mixing.

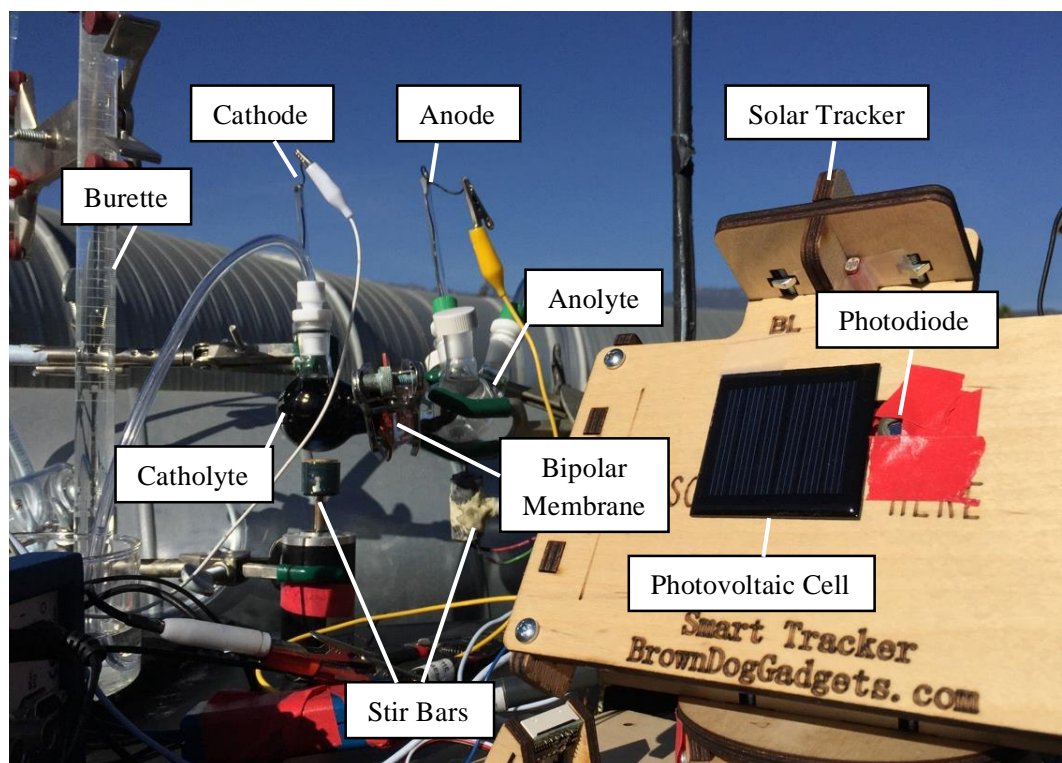
The apparatus was then rotated back upright, and the valve to the pressure gauge was opened and the resulting pressure from the reaction was read. The headspace of the apparatus was estimated to be 10.4 mL, based on measuring the amount of water needed to fill the chamber.



**Figure S1.** A schematic illustration of the full process flow.



**Figure S2.** Current density of the  $V^{3+/2+}(aq, H_2SO_4) | KOH(aq)$  cell as vanadium was charged at various potentials.

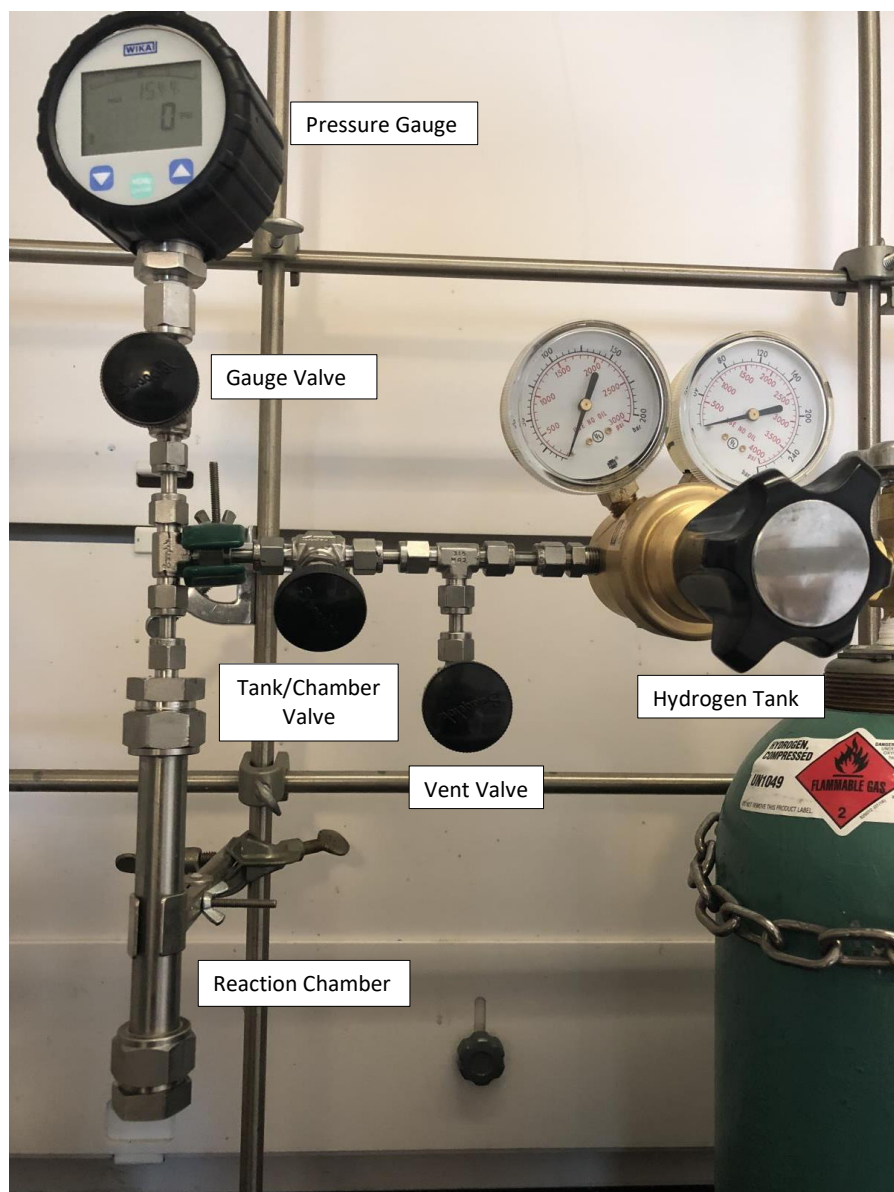


**Figure S3.** Outdoor setup of the  $V^{3+/2+}(aq, H_2SO_4) | KOH(aq)$  cell coupled with a photovoltaic cell affixed to a solar tracker.

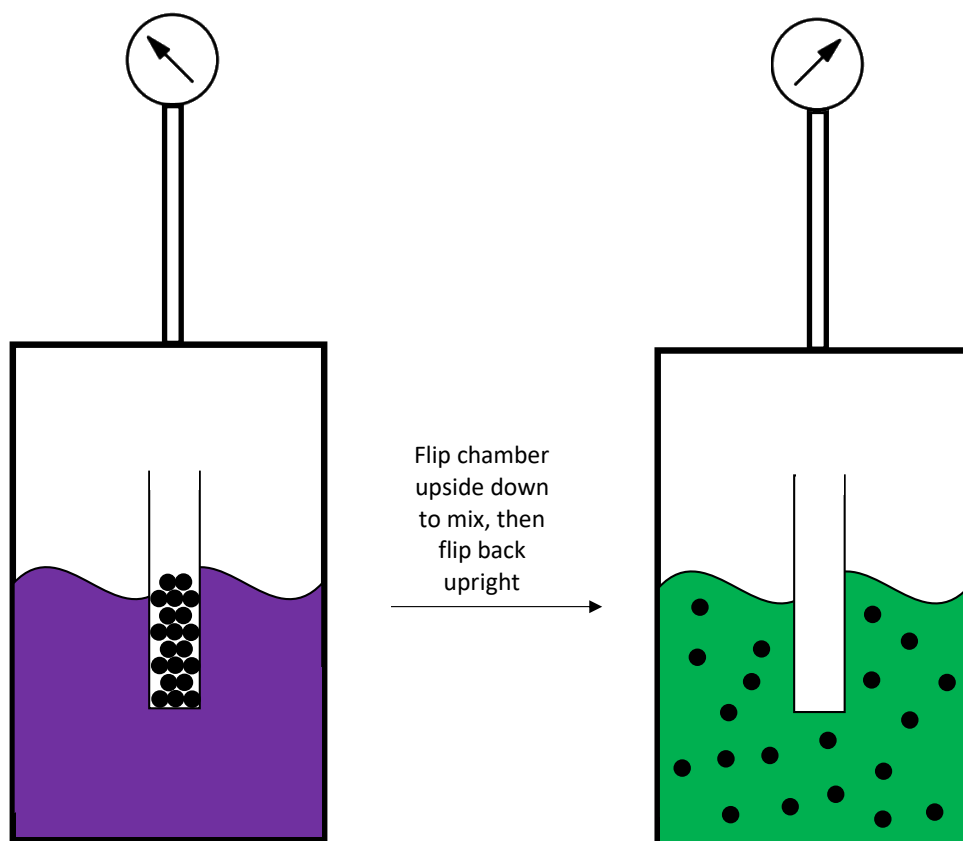


**Figure S4.** Hydrogen collection from  $V^{2+}$  stirred with the  $Mo_2C$  catalyst.





**Figure S5.** Pressurization experiment apparatus. With the vent valve closed and the gauge valve and tank/chamber valve open, the hydrogen tank was opened and adjusted so the pressure gauge read the desired pressure. The tank/chamber valve and hydrogen tank were then closed, and the vent valve was opened to vent the intermediate chamber. The hydrogen tank was then disconnected, and then the apparatus connected to the reaction chamber was flipped to allow catalyst to mix with catholyte, before being flipped back upright to read the resulting pressure.



**Figure S6.** Schematic of catalyst introduction to the catholyte in the pressurized stainless-steel apparatus reaction chamber. The catalyst only mixed with the catholyte (purple) when the apparatus was flipped upside down, causing hydrogen to be produced and measured by the pressure gauge. The apparatus was flipped right side up after the catalyst was mixed with the catholyte.

**Table S1.** Bipolar membrane potential loss and crossover rates comparison

pH	Authors	Electrolytes	$V_{\text{membrane, loss}}$	Crossover rates	Ref
Extreme pHs	Vermaas, Wiegman, Nagaki & Smith	1 M $\text{H}_2\text{SO}_4$ (pH= 0) / 1 M $\text{KOH}$ (pH= 14)	19 mV @ 10 mA $\text{cm}^{-2}$	N.A	2
	Reiter, White & Ardo	1 M $\text{H}_2\text{SO}_4$ (pH= 0) / 1 M $\text{KOH}$ (pH= 14)	58 mV@ 10 mA $\text{cm}^{-2}$	N.A.	3
	Ho, Zhou, Han, Sullivan, Karp, Lewis & Xiang	2.0 M $\text{H}_2\text{SO}_4$ (pH = - 0.16) / 2.5 M $\text{KOH}$ (pH = 14.21)	81 mV@ 10 mA $\text{cm}^{-2}$	$f_{\text{H}^+}=93.9\%$ $f_{\text{OH}^-}=98.2\%$ (@ 10 mA $\text{cm}^{-2}$ )	This work
	Ho, Zhou, Han, Sullivan, Karp, Lewis & Xiang	2.0 M $\text{H}_2\text{SO}_4$ , 0.36 M $\text{V}_2(\text{SO}_4)_3$ (pH = -0.16) / 2.5 M $\text{KOH}$ (pH = 14.21)	18 mV@ 10 mA $\text{cm}^{-2}$	$f_{\text{H}^+}=92.1\%$ $f_{\text{OH}^-}=99.5\%$ (@ 10 mA $\text{cm}^{-2}$ )	This work
Near-neutral pHs	Vermaas, Wiegman, Nagaki & Smith	1 M $\text{KPi}$ (0.55 M $\text{KH}_2\text{PO}_4$ , 0.45 M $\text{K}_2\text{HPO}_4$ ) (pH=7)	797 mV@ 10 mA $\text{cm}^{-2}$	N.A.	2
	Vargas-Barbosa, Geise, Hickner & Mallouk	1.75 M $\text{NaH}_2\text{PO}_4$ / 1.75 M $\text{K}_2\text{HPO}_4$ (pH=6.86)	845 mV @ 10 mA $\text{cm}^{-2}$	N.A.	4
	Sun, Liu, Chen, Verlarge, Lewis & Xiang	1 M $\text{H}_2\text{SO}_4$ (pH= 0) / 0.5 M $\text{KBi}$ (pH=9.3)	450 mV @ 4.36 mA $\text{cm}^{-2}$	$f_{\text{H}^+}=97.5\%$ $f_{\text{OH}^-}=92.3\%$ (@ 4 mA $\text{cm}^{-2}$ )	1
	Zhou, Liu, Sun, Chen, Verlage, Francis, Lewis & Xiang	2.8 M $\text{KHCO}_3$ (pH=8.0) / 1.0 M $\text{KOH}$ (pH=13.7)	508 mV@ 10 mA $\text{cm}^{-2}$	$f_{\text{H}^+}>90\%$ $f_{\text{OH}^-}>95\%$ (@ 8 mA $\text{cm}^{-2}$ )	5

**Table S2.** ICP-MS measurement for vanadium species crossover the bipolar membrane

	Concentration of vanadium species ( $\mu\text{M}$ ) using measured calibration data
Calibration sample A: 1 $\mu\text{M}$ vanadium species	1.29
Calibration sample B: 10 $\mu\text{M}$ vanadium species	10.95
Calibration sample C: 50 $\mu\text{M}$ vanadium species	49.30
Calibration sample D: 100 $\mu\text{M}$ vanadium species	104.48
Calibration sample E: 500 $\mu\text{M}$ vanadium species	499.15
Anolyte before operating at 10 $\text{mA cm}^{-2}$ for 24 h	101.82
Anolyte after operating at 10 $\text{mA cm}^{-2}$ for 24 h	110.99

All the samples were in 2.5 M KOH, and diluted by 80 times in  $\text{HNO}_3$  solution for neutralization before the ICM-MS characterization.

Vanadium concentration in the anolyte enhancement was  $110.99 - 101.82 = 9.17 \mu\text{M}$ , and then be converted into  $J_{\text{V}^{3+/2+}} = 0.226 \mu\text{A cm}^{-2}$ .

**Table S3.** Comparison of overpotentials at an operating current density of 10 mA cm<sup>-2</sup> in three different systems

System	A	B	C
Cathode	37	266	266
Membrane	~ 70	~ 70	~ 70
Anode	270	244	379
Solution/Electrolyte IR drops	~100	~100	~100
Total voltage	~1.70 V	~2.37 V	~2.32 V

Unit: mV (unless noted otherwise)

System A: Pt/1.0 M H<sub>2</sub>SO<sub>4</sub>/Nafion/1.0 M H<sub>2</sub>SO<sub>4</sub>/IrO<sub>x</sub>

System B: Carbon cloth/2.0 M H<sub>2</sub>SO<sub>4</sub> 0.36 M V<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/Nafion/1.0. M H<sub>2</sub>SO<sub>4</sub> 0.10 M Ce<sup>3+</sup>/Pt

System C: Carbon cloth/2.0 M H<sub>2</sub>SO<sub>4</sub> 0.36 M V<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/BPM/2.0 M KOH/Ni mesh

## Reference

(1) Sun, K.; Liu, R.; Chen, Y.; Verlage, E.; Lewis, N. S.; Xiang, C. A Stabilized, Intrinsically Safe, 10% Efficient, Solar-Driven Water-Splitting Cell Incorporating Earth-Abundant Electrocatalysts with Steady-State pH Gradients and Product Separation Enabled by a Bipolar Membrane. *Adv. Energy Mater.* **2016**, 6 (13), 1600379.

(2) Vermaas, D. A.; Wiegman, S.; Nagaki, T.; Smith, W. A. Ion Transport Mechanisms in Bipolar Membranes for (Photo)electrochemical Water Splitting. *Sustainable Energy Fuels* **2018**, 2 (9), 2006-2015.

- (3) Reiter, R. S.; White, W.; Ardo, S. Communication-Electrochemical Characterization of Commercial Bipolar Membranes under Electrolyte Conditions Relevant to Solar Fuels Technologies. *J. Electrochem. Soc.* **2016**, *163* (4), H3132-H3134.
- (4) Vargas-Barbosa, N. M.; Geise, G. M.; Hickner, M. A.; Mallouk, T. E. Assessing the Utility of Bipolar Membranes for use in Photoelectrochemical Water-Splitting Cells. *ChemSusChem* **2014**, *7* (11), 3017-3020.
- (5) Zhou, X.; Liu, R.; Sun, K.; Chen, Y.; Verlage, E.; Francis, S. A.; Lewis, N. S.; Xiang, C. Solar-Driven Reduction of 1 atm of CO<sub>2</sub> to Formate at 10% Energy-Conversion Efficiency by Use of a TiO<sub>2</sub>-Protected III–V Tandem Photoanode in Conjunction with a Bipolar Membrane and a Pd/C Cathode. *ACS Energy Lett.* **2016**, *1* (4), 764-770.